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The effect of oxygen exposure on pentacene electronic structure

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Abstract. We use ultraviolet photoelectron spectroscopy to investigate the effect of oxygen and air exposure on the electronic structure of pentacene single crystals and thin films. It is found that O_2 and water do not react noticeably with pentacene, whereas singlet oxygen/ozone readily oxidize the organic compound. Also, we obtain no evidence for considerable p-type doping of pentacene by O_2 at low pressure. However, oxygen exposure lowers the hole injection barrier at the interface between Au and pentacene by 0.25 eV, presumably due to a modification of the Au surface properties.

PACS. 73.20.Hb Impurity and defect levels; energy states of adsorbed species – 79.60.Fr Polymers; organic compounds – 79.60.Jv Interfaces; heterostructures; nanostructures

1 Introduction

Pentacene is *the* prototypical conjugated organic molecule for use as active material in novel electronic devices, such as thin-film field effect transistors [1,2]. Therefore, extensive research efforts are being undertaken to investigate fundamental and applied aspects of pentacene thin-film and single-crystal properties. The interplay between thin-film structure/morphology and measured charge carrier mobility is of particular interest [3–5]. However, a reliable comparison between experimental results obtained in different laboratories is often hampered by the variation of sample preparation and the environmental conditions for mobility measurements [1,6,7]. Another issue is long-term stability of devices made from organic materials, as oxidation is believed to be a major reason for early device failure [8,9]. It has been observed that the measured conductivity of pentacene single crystals depends on the residual oxygen or air pressure [10]. It was shown that oxygen can diffuse into pentacene, and readily diffuses out again after re-evacuation [10]. When exposing a pentacene single crystal to dry air at atmospheric pressure the current through the crystal increased by a factor of 1.6 (measured in dark) or even 4 (measured under illumination) compared to the same crystal kept in a vacuum of 10^{-5} mbar. On a timescale of ca. 150 min, the maximum effect is observed and afterwards a plateau is reached, as equilibrium is established [10]. The time constant is diffusion limited. Still to be addressed is the nature, on a molecular scale, of oxygen-induced changes in charge transport properties. It needs to be established to what extent and under which experimental conditions these changes are reversible. Additionally, it has been proposed that oxygen may create new (chemical) species in pentacene films, (*e.g.*, 6,13-pentacenequinone or an endoperoxide). Consequently, a movement of the Fermi level (E_F) in the organic film towards the highest occupied molecular orbital (HOMO) is predicted, displaying p-type behavior of the organic semiconductor [11,12]. Our approach to resolve some of the above questions consists in using ultraviolet photoelectron spectroscopy (UPS) to follow changes in the E_F-position of pentacene single crystals and thin films before and after exposure to oxygen and to air.

2 Experimental

Photoemission experiments were performed at the endstation SurICat (beamline PM4) at the synchrotron light source BESSY GmbH. The ultrahigh vacuum (UHV) system consists of interconnected sample preparation (base pressure: 1×10^{-8} mbar) and analysis (base pressure: 5×10^{-10} mbar) chambers. Sample transfer between chambers proceeded without breaking UHV conditions. The excitation energy for UPS was 25 eV, and the spectra

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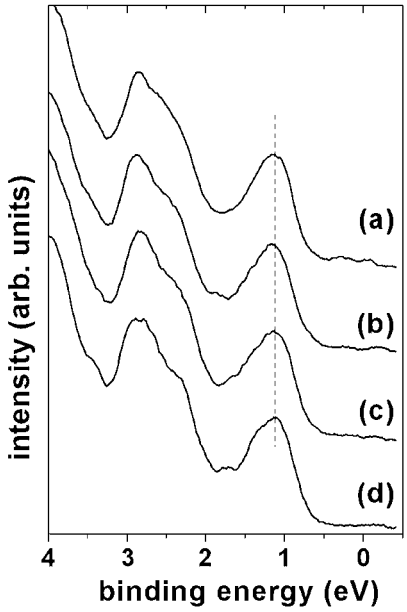

Fig. 1. UPS spectra of a pentacene single crystal measured under the following conditions (and in this time sequence): (a) 3×10^{-8} mbar partial O_2 pressure, (b) 2×10^{-9} mbar total residual pressure, (c) 3×10^{-8} mbar partial O_2 pressure after exposure to 5×10^{-6} mbar O_2 for 30 min, and (d) again at 2×10^{-9} mbar total residual pressure.

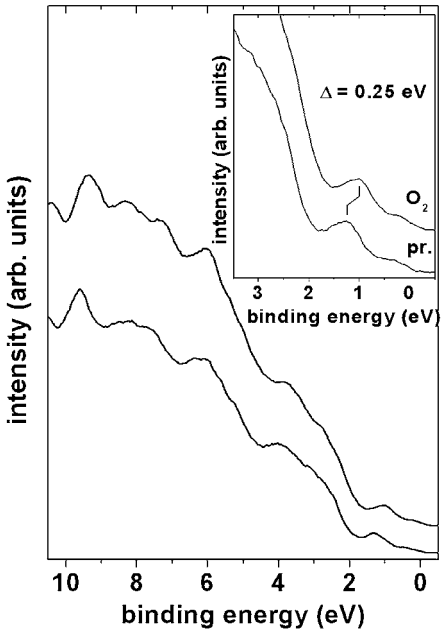

Fig. 2. Extended BE scale UPS spectra of 12 nm pentacene on Au before (pristine; bottom curve) and after (upper curve) exposure to one atmosphere of O_2 for 60 min. Inset: close-up of the near-E_F region, indicating the rigid shift Δ.

were collected with a hemispherical electron energy analyzer (Scienta SES 100) with an energy resolution of 140 meV (80%–20% intensity drop at the Au Fermi edge). Pentacene single crystals were grown *ex situ* using the method described in reference [4]. They were mounted on metal sample holders with conducting adhesive tape, and cleaved *in situ* (in the preparation chamber) by peeling off adhesive tape stuck to the crystal surface. Pentacene molecules crystallize in a layered structure with a herringbone arrangement within the layers [13]. The herringbone arrangement is such that the hydrogen orbitals of one molecule interact strongly with the π-system of neighboring molecules. The interactions between the layers are less strong, as they are van der Waals interactions. Therefore, the crystal will cleave easily along the *a-b* plane (perpendicular to the c^* direction). Single-crystal samples were irradiated with a laser (frequency-doubled Nd:YVO_4, 532 nm, 40 mW) during UPS measurements, in order to avoid charging [14,15] of the thick crystals (ca. 20 μm).

Pentacene (Aldrich, gradient-sublimation cleaned two times) evaporation was realized in the preparation chamber from a resistively heated pinhole source. The films' mass thickness was monitored with a quartz microbalance. As substrates we used *in situ* sputtered Au films (on silicon), native silicon oxide (Si wafer cleaned in H_2O_2(30%) + H_2SO_4(99.99%) (3 : 1), etched with HF, and re-oxidized by exposure to oxygen at atmospheric pressure for one hour), and *ex situ* cleaved highly oriented pyrolytic graphite (HOPG; GE Advanced Ceramics).

Exposure of single crystal samples to oxygen (purity 5N) was done in the analysis chamber *via* a leak-valve. Thin-film samples were exposed to oxygen and air (both up to atmospheric pressure) in the preparation chamber. All sample preparation steps and measurements were performed at room temperature.

3 Results and discussion

The valence region UPS spectra (Fig. 1) recorded on a pentacene single crystal under different residual oxygen pressures during the measurement and total oxygen exposure clearly show that there is no influence of molecular oxygen on the position of the energy levels (at the given conditions). We note that the exposure to oxygen at 10^{-6} mbar for one second is sufficient for the (hypothetical) formation of a complete O_2 monolayer. If crystalline pentacene were prone to undergo rapid oxidation, the dosing conditions used here would allow for the detection of such, since UPS is highly surface sensitive. A reaction of pentacene with electron withdrawing oxygen would result in a loss of conjugation, which would be visible in a UPS spectrum as a decrease in the relative intensity and shift towards higher binding energy of the emission derived from the HOMO [15] (the peak at 1.1 eV binding energy in Fig. 1). All four spectra in Figure 1 exhibit the same characteristic photoemission features of pentacene, comparable to previous reports [16,17]. If "doping" (*i.e.*, p-type) of pentacene by O_2 were the case (to a significant degree), a clear shift of all levels towards lower binding energy (BE) would be observed [12,18]. While changes in conjugation (due to a chemical reaction) would be difficult to be seen for concentrations smaller than a few percent, energy

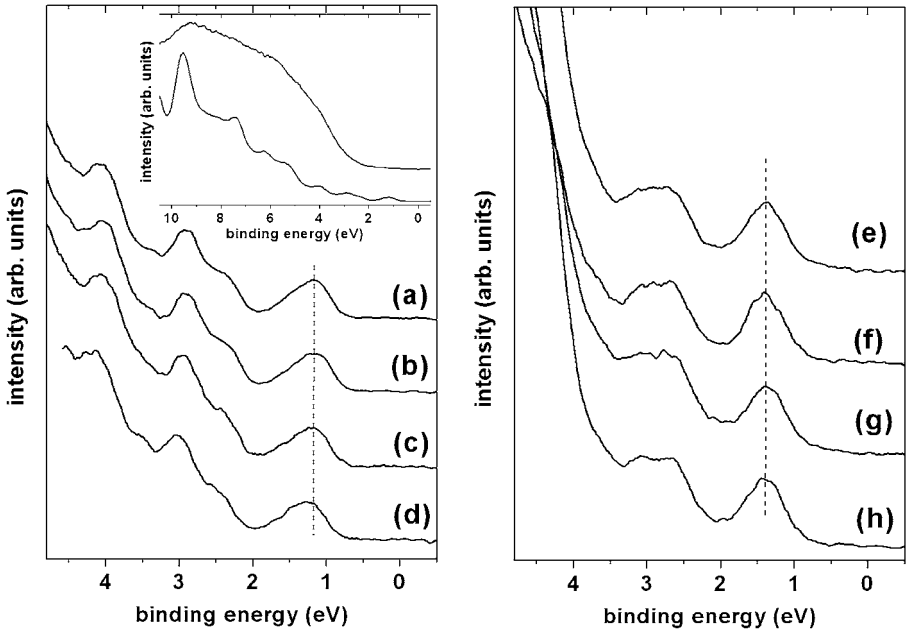

Fig. 3. UPS spectra of 12 nm pentacene films on SiO_2 (left-hand side) and HOPG (right-hand side). (a) and (e): pristine. (b) and (f): after exposure to one atmosphere O_2 for 30 min (in dark). (c) and (g): after additional exposure to one atmosphere O_2 for 120 min (with visible light). (d) and (h): after additional exposure to ambient air for 60 min (with visible light). Inset: extended BE scale UPS spectra of the pristine pentacene film on SiO_2 (bottom curve), and after exposure to ambient air for 15 min with UV irradiation (top curve).

shifts due to doping can readily be seen for much smaller concentrations (below 0.3% [18]). However, the total *in situ* exposure of the single crystal to O_2 was rather limited (up to a pressure of 3×10^{-8} mbar; for experimental limitations). As the time required for oxygen molecules to insert in the pentacene crystal bulk is on the order of tens of minutes even at atmospheric pressure (the time constant for 15 μm thick crystals is approximately 100 minutes [10]), we could not expect to see noticeable changes in the energy position of the spectrum. Therefore, we have continued on *in situ* deposited thin films of pentacene.

A pentacene film of 12 nm nominal thickness was deposited onto *in situ* sputtered polycrystalline Au. The corresponding UPS spectrum is shown on a wide energy range in Figure 2 (bottom curve), and as a close-up in the figure inset. The Au Fermi edge can still be discerned, since pentacene exhibits pronounced island growth on Au [17]. The low BE onset of the highest occupied molecular orbital (HOMO) is 0.8 eV below the Fermi level (E_F), consistent with earlier reports [17,19]. After exposure to O_2 at atmospheric pressure for one hour, the entire UPS spectrum was shifted 0.25 eV towards lower BE (Fig. 2, upper spectrum, and inset) but the lineshape remained unchanged. This result would be consistent with p-type doping of pentacene by oxygen that remains intercalated within the organic layer after re-evacuation. However, it has been suggested by Seki and Ishii [20] that oxygen adsorption below the organic film on the metal substrate surface changes its work function (ϕ). Therefore, the shift seen in Figure 2 may be related to this change of substrate ϕ and/or a shift of the pentacene molecular levels due to doping. The only way to differentiate between the two mechanisms is the use of substrates which are not influenced by oxygen. The surfaces of silicon oxide (SiO_2) and HOPG are suitable for the present purpose.

Figure 3 shows UPS spectra of nominally 12 nm thick, pristine pentacene films on SiO_2 (a) and HOPG (e). These two spectra differ in the relative photoemission intensities from some molecular levels, as one can see clearly for the feature at ca. 3 eV BE in particular. This is due to the fact that the long molecular axis of pentacene is oriented almost vertically on SiO_2 (when the film is grown at room temperature [21]), while it is presumably parallel to the surface of HOPG [22]. It is known that measured photoemission intensities depend strongly on molecular orientation [23]. The energy spacing of emission features in both films are identical, thus we can conclude that intact pentacene is present on both surfaces.

These two films were exposed to one atmosphere of pure oxygen in dark for 30 min (Fig. 3(b) and (f)). Subsequently, the samples were exposed to one atmosphere of pure oxygen for 120 min (Fig. 3(c) and (g)), this time irradiated with visible light (to test the influence of pentacene optical excitation during exposure) from a halogen lamp (cutoff wavelength of the experimental chamber glass window: 300 nm). In the next step, both samples were exposed to ambient air for 60 min (Fig. 3(d) and (h)), again with visible-light irradiation. Finally, exposure to ambient air for 15 min proceeded, with the samples being additionally exposed to ultraviolet (UV) light (inset of Fig. 3) from a low-pressure Hg-lamp (placed ca. 10 cm away from the samples). Note that the applied exposure times are

sufficient for complete diffusion of O_2 through the thin film (as mentioned above for thick single crystals [10]), and that after each exposure the samples were brought back to UHV conditions for the UPS measurements.

Most notably, spectra (a)–(d) and (e)–(h) of Figure 3 are —within the experimental error— virtually identical in both energy position and lineshape, regardless of treatment. The essence of these experimental results is that molecular oxygen and also water (from air) do not react irreversibly with pentacene (on the timescale of our experiments), as long as they come into contact in dark or under visible light. The surface sensitivity of UPS would unmistakably allow for the identification of such a reaction. We can furthermore conclude that optically excited pentacene (the optical gap of pentacene is 1.85 eV [24], thus well contained in the spectrum of the halogen lamp used here) is not sufficient to promote a reaction. Oxygen possibly diffused into pentacene at atmospheric pressure appears to diffuse out again rapidly after re-evacuation, and does not lead to irreversible changes (detectable by UPS) in the electronic structure, like, *e.g.*, p-type doping (as might have been suspected from the experiment with the Au substrate). Yet, charge traps predicted in several works may be present [9,12], but at such low density that the Fermi level position in pentacene is not affected. The shift of $\leqslant 0.1$ eV observed for spectrum (d) in Figure 3 might point towards an effect of water adsorption on the SiO_2 substrate properties. We can rule out that pentacene itself is affected, since no shift is seen for pentacene/HOPG (spectrum (h)).

In contrast, the inset of Figure 3 demonstrates that the exposure of pentacene to air in the presence of UV light leads to a rapid reaction of pentacene, most probably an oxidation by singlet oxygen and/or ozone (produced by the UV light). Unfortunately, the reaction product is ill-defined, as can be seen from the featureless spectrum (upper curve in the inset of Fig. 3). Essentially the same spectrum was observed for the pentacene/HOPG after air/UV exposure (spectrum not shown). This result is corroborated by infrared spectroscopy experiments under similar conditions, where only one new broad absorption attributed to C-O vibrations could be observed after pentacene oxidation [25].

By the comparison of our results obtained on three different substrates we can clearly differentiate between doping of pentacene (*not observed* under the present experimental conditions) and a modification of the substrate properties (*observed* for the Au substrate) due to oxygen exposure. We cannot exclude that oxygen- or water-induced changes occur at higher pressures (still reversible), which we could not achieve because of intrinsic limitations of our experimental method. The implication for devices comprising pentacene and Au contacts (*e.g.*, field effect transistors [12]) is that upon exposure of the devices to oxygen/air a considerable lowering (increase) of the hole (electron) injection barrier from Au into pentacene occurs (*i.e.*, from 0.8 eV to 0.55 eV for holes), which is not caused by doping.

4 Conclusion

In extensive tests we have observed no irreversible reaction of pentacene with molecular oxygen and water on the timescale of a few hours, even if pentacene is optically excited. More importantly, it is found that oxygen diffusion through pentacene thin films (and single-crystals surfaces) is reversible, and does not leave behind —after re-evacuation— electrically active electronic states that would lead to doping of the organic bulk material. This is evidenced by a lack of energy shifts in UPS spectra of pentacene before and after exposure to O_2 and to air. Instead, it was found that the hole injection barrier at the Au/pentacene interface is lowered by oxygen exposure.

Finally, it was demonstrated that rapid oxidation of pentacene occurs in air only in the presence of UV light, probably due to the formation of highly reactive singlet oxygen and/or ozone.

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